ABSTRACT OF THE DISCLOSURE

6α-fluorpregnanes (I), where the dotted line between positions 1 and 2 represents a single or double bond; R1 is OH, $OCOR_2$, X, SO_3R_3, or an $(R_7)(R_8)(R_9)SiO$- group, where X is halogen, R_2 and R_3 are C_{1-6} alkyl or phenyl optionally substituted by C_{1-4} alkyl, and R_7, R_8 and R_9, equal or different, are C_{1-6} alkyl or phenyl optionally substituted by C_{1-4} alkyl, can be obtained by means of a high stereoselectivity process comprising reacting a 3-(trisubstituted)silyloxy-pregna-3,5-diene (IV) with a fluorinating agent selected among N-fluorosulfonimides and N-fluorosulfonamides. The 6α-fluorpregnanes (I) are intermediates for the synthesis of steroids useful as anti-inflammatory and anti-asthmatic agents.